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**Distribution pattern of legacy and “novel” brominated flame retardants in different particle size fractions of indoor dust in Birmingham, United Kingdom**

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**ABSTRACT**

This study investigates the particle size distribution of eight polybrominated diphenyl ethers (PBDEs) and five “novel” brominated flame retardants (NBFRs) in settled house dust. Elevated surface dust (ESD) and floor dust (FD) were collected from 5 homes in Birmingham, UK, yielding a total of 10 samples. Each sample was fractionated into three different particle sizes: 125-250  $\mu\text{m}$  (P1), 63-125  $\mu\text{m}$  (P2) and 25-63  $\mu\text{m}$  (P3). Non-fractionated bulk dust samples (BD) were also analysed. BDE-209 predominated, comprising an average 74.3%, 77.3%, 69.2%, and 62.7%  $\Sigma\text{BFRs}$  of BD, P1, P2 and P3 respectively.  $\Sigma_5\text{NBFRs}$  contributed 24.2%, 21.5%, 29.0% and 35.3%  $\Sigma\text{BFRs}$ , while  $\Sigma_7\text{tri-hepta-BDEs}$  represented 1.5%, 1.2%, 1.7%, and 2.0%  $\Sigma\text{BFRs}$ . BEH-TEBP was the predominant NBFR contributing 76.9%, 75.1%, 83.1%, and 83.9%  $\Sigma\text{NBFRs}$  in BD, P1, P2 and P3 respectively; followed by DBDPE which contributed 20.1%, 21.9%, 14.1% and 13.9%  $\Sigma\text{NBFRs}$ . EH-TBB, BTBPE and PBEB were the least abundant NBFRs. Concentrations of  $\Sigma_7\text{tri-hepta-BDEs}$  and BEH-TEBP in P3 exceeded significantly ( $P < 0.05$ ) those in P2, with those in P2 exceeding significantly those in P1. In contrast, no significant differences were found between concentrations of BDE-209, EH-TBB, BTBPE, and DBDPE in different particle size fractions. Concentrations of  $\Sigma_7\text{tri-hepta-BDEs}$ , BDE-209, and BEH-TEBP in ESD exceeded significantly those in FD ( $P < 0.05$ ). Normalising BFR concentrations to organic carbon content, did not alter these findings. This suggests that differences in BFR concentrations between different particle size fractions are caused by variations in particle surface area to volume ratio, rather than by variations in organic carbon content.

## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants (BFRs) added to several polymers used in various consumer products such as electronics, textiles, and polyurethane foams. They are blended physically with – rather than chemically bound to – polymeric materials, which likely lead them to migrate into the environment (WHO, 1997; USEPA, 2010 Alaei et al., 2003). PBDEs are persistent and bioaccumulative toxicants, with available information suggesting that they affect negatively the nervous system, the liver and the thyroid system (NICNAS, 2007; USEPA, 2008; Shaw et al., 2009; Noyes et al., 2010; Yu et al., 2011; Johnson et al., 2013; Yang et al., 2014; Zhang et al., 2014; Fang & Stapleton, 2014). Hence, their manufacture and new use is now banned or severely restricted in many jurisdictions, and they are listed – or in the case of the Deca-BDE product nominated for listing - under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2008; 2013a; b). Such bans and restriction on the use of established BFRs like PBDEs has resulted in increased production of several other BFRs collectively referred to here as novel brominated flame retardants (NBFRs). These NBFRs display physicochemical properties similar to those of established BFRs (Covaci 2011; EFSA, 2012), and there is growing concern about increasing environmental contamination with NBFRs (Shi et al., 2009; Shoeib et al., 2012; Ali et al., 2013; Fromme et al., 2014; Poma et al., 2014; Hassan et al., 2015; Al-Omran and Harrad in press; Newton et al., 2015) and their potential negative health effects (Johnson et al., 2013).

Among the various human exposure pathways, ingestion of indoor settled dust appears to represent a major pathway for human exposure to BFRs in North America and Europe, particularly for young children as a result of normal hand-to-mouth activity (Besis and Samara 2012). Indoor settled dust refers to “particles in building interiors that have settled onto objects, surfaces, floors, and carpeting. These particles may include soil particles that have been tracked or blown into the indoor environment from outdoors as well as organic matter” (USEPA, 2011).

In general, indoor dust falls into a wide range of particle size fractions ranging from  $< 2.5 \mu\text{m}$  to over  $2 \text{ mm}$  and possessing organic contents between 5% and 95% (Morawska and Salthammer, 2003). However, for human exposure assessment, dust particles  $< 250 \mu\text{m}$  are considered of particular concern (USEPA, 2000; 2003), as these have been proposed as those

most likely to stick to hands and be ingested (Duggan and Inskip, 1985; Hee et al., 1985; Edwards et al., 1999; Yamamoto et al., 2006).

A large and growing body of literature has investigated human exposure to BFRs via indoor dust using a disparate range of particle sizes, for example,  $< 75 \mu\text{m}$  (Xu et al., 2015),  $< 100$  (Kang et al., 2011),  $< 125 \mu\text{m}$  (Wu et al., 2007),  $< 150 \mu\text{m}$  (Wilford et al., 2005; Shoeib et al., 2012; Whitehead et al., 2012), 25-250  $\mu\text{m}$  (Al-Omran and Harrad, in press),  $< 500 \mu\text{m}$  (Allen et al., 2008; Wang et al., 2010), 25-500  $\mu\text{m}$  (Harrad et al. 2008a; 2008b; Muenhor et al., 2010; Brommer et al., 2012),  $< 1000 \mu\text{m}$  (Suzuki et al., 2006),  $< 2000 \mu\text{m}$  (Gevao et al., 2006) and all fractions (Takigami et al., 2008). Early studies on polycyclic aromatic hydrocarbons (PAHs) and pesticides in indoor dust and airborne particles, indicate that, due to the inverse relationship between particle size and specific surface area, levels of these pollutants increase gradually with decreasing particle size (Lewis et al., 1999; Sygiyama et al., 2000).

The first study to investigate PBDE concentrations as a function of dust particle size was ten years later (Wei et al., 2009). By analysing four different dust fractions (250- 420  $\mu\text{m}$ , 150- 250  $\mu\text{m}$ , 75-150  $\mu\text{m}$ , and  $< 75 \mu\text{m}$ ) in indoor dust (1 car and 2 homes), Wei et al., (2009) found that PBDE levels in car dust were inversely related to particle size, while they were comparable in homes. Limited studies since, suggest BFR concentrations are influenced significantly by dust particle size. Kefeni et al., (2014) reported that of the PBDEs detected in dust particles  $< 250 \mu\text{m}$  from 2 homes and two offices; 93.4% were associated with particles  $< 150 \mu\text{m}$ . In a similar study, Chao et al., (2014) found no significant difference in concentrations of  $\Sigma_{28}\text{PBDE}$  in different particle sizes of house dust and electronic dust. Based on analysis of office dust particle size fractions, Cao et al., (2013) reported some variation in concentrations of PBDEs with particle size. Concentrations of tri-hexa PBDEs were highest in the 74-100  $\mu\text{m}$  and 100-200  $\mu\text{m}$  particle size fractions, those of hepta-PBDEs were greatest in 200-300  $\mu\text{m}$  and 300-400  $\mu\text{m}$  fractions, octa- and deca-PBDE concentrations peaked in particles  $< 50 \mu\text{m}$ , while 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) was highest in the 50-74  $\mu\text{m}$  and 75-100  $\mu\text{m}$  size range. In a subsequent study by the same authors, Cao et al., (2014) found that in several non-domestic microenvironments, BDE-209 showed higher levels in coarser particles in kindergartens (500-900  $\mu\text{m}$ ) and dormitories (900-2000  $\mu\text{m}$ ). Moreover, BFR concentrations did not increase constantly with decreasing particle size. Instead, the variation of concentrations with particle size was multi-modal, with the highest

levels associated with particle sizes around 900, 100, and 10  $\mu\text{m}$  (Cao et al., 2014). A later study revealed no significant variation in concentrations of HBCDs between different particle size fractions (Cao et al., (2015). Other studies have used forensic microscopy to show that the highest levels of BFRs are present in particles with different morphology, containing more fibre-like material (Wei et al., 2009; Cao et al., 2013).

From the above, it is apparent that while concentrations of many BFRs vary according to the dust particle size fraction, the exact nature of this variation remains unclear. Moreover, the reasons for such variation have yet to be conclusively elucidated. A related issue is whether BFR concentrations differ significantly between floor and elevated surface dust. We hypothesised previously in a study of house dust from Basrah, Iraq, that the existence of such differences would suggest a need to sample both dust sample types, in order to fully reflect exposure of the room occupants (Al-Omran and Harrad, in press). In that same study, we found that differences in the organic carbon content of dust samples, could not explain the higher concentrations of PBDEs and NBFRs detected in elevated surface dust compared to floor dust in the same rooms. It instead seems more plausible that BFR concentrations will be greater in dust particles with a greater surface area to mass ratio, a hypothesis consistent with the higher proportion of finer particles found in elevated surface compared to floor dust in Basrah (Al-Omran and Harrad, in press).

This study therefore reports concentrations of eight PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and five NBFRs: pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenylethane (DBDPE) in both elevated surface dust and floor dust from Birmingham, UK. Each dust sample is separated into three different particle size fractions (125-250  $\mu\text{m}$ , 63-125  $\mu\text{m}$ , and 25-63  $\mu\text{m}$ ). BFR concentrations are reported both as dry weight and normalised to dust organic carbon content. These data are used to test our hypotheses that: (a) BFR concentrations in elevated surface dust will exceed those in floor dust; (b) BFR concentrations will increase with decreasing particle size; and (c) variations in dust organic carbon content cannot account for any variations in BFR concentrations between different particle size fractions.

## **2. Materials and methods**

### **2.1. Chemicals and standards**

Native and labelled PBDEs (BDE-28, BDE-47, BDE-77, BDE-99, BDE-100, BDE-128, BDE-153, BDE-154, BDE-183, BDE-209 and  $^{13}\text{C}$ -BDE-209) and NBFRs (PBEB, EH-TBB, BTBPE,  $^{13}\text{C}$ -BTBPE, BEH-TEBP,  $^{13}\text{C}$ -BEH-TEBP and DBDPE) standards were purchased from Wellington Laboratories Inc. Guelph, Canada as stock solutions in iso-octane, except BDE-209 and  $^{13}\text{C}$ -BDE-209 which were purchased as stock solutions in nonane. The recovery determination standard PCB-129 in hexane was purchased from Qmx Laboratories, UK. The purity of all standards is > 98%. Ethyl acetate (EA), Acetone (Ac), *n*-Hexane, dichloromethane (DCM), iso-octane, phosphoric acid and sulfuric acid were obtained from Fisher Scientific UK Ltd. All solvents used during analysis were of HPLC analytical grade. Silica gel (pore size 60 Å, 70-230 mesh) was purchased from Sigma Aldrich, Switzerland, anhydrous sodium sulphate was obtained from Sigma Aldrich, USA, and Florisil® (particle size 60-100) acquired from Fluka, USA. Sodium bicarbonate was purchased from Nacalai Tesque, Japan, and sucrose (analytical reagent grade) was purchased from Fisher Scientific, UK. The standard reference material (SRM 2585, "Organic Contaminants in House Dust") was purchased from the National Institute of Standards and Technology (NIST) Gaithersburg, MD, USA. Finally, ISOLUTE amino propyl columns, SPE cartridges and frits were purchased from Biotage (Uppsala), Sweden.

### **2.2. Sampling and sample preparation**

Between September 2013 and February 2014, elevated surface dust (ESD) and floor dust (FD) was collected from the living room and two bedrooms in each of 5 homes in Birmingham, UK. ESD and FD was collected every month for 4 months in two homes ( $n = 16$ ), and for 5 months in three ( $n = 30$ ). In order to provide sufficient dust mass for fractionation (especially necessary for ESD for which dust mass loadings in these UK homes were very low), the ESD and FD samples from each home were then combined to yield two bulk dust samples (one ESD and one FD) from each of the 5 homes. Samples were collected using a handheld vacuum cleaner (DIRT DEVIL-DDMHH1-1100W), according to a clearly defined standard protocol (Harrad et al., 2008a). 1 m<sup>2</sup> of carpeted floor was vacuumed for 2 min and, in the case of bare floor, 4 m<sup>2</sup> for 4 min using 25 µm pore size nylon sample socks (Allied Filter Fabric Pty Ltd, Australia) that were mounted in the furniture attachment tube of the vacuum cleaner. Elevated surfaces (typically between 50-150 cm height) were vacuumed

for 2-4 min depending on the surface area. After sampling, socks were closed with a twist tie, sealed in plastic bags and stored at  $-20^{\circ}\text{C}$ . Before sampling, the furniture attachment and the vacuum tubing were cleaned thoroughly using an isopropanol-impregnated disposable wipe and dried between collections. Information on the potential influences on BFR contamination such as: the number and type of putative sources like electronic devices, foam-filled furniture and floor material, ventilation system, house cleaning method was recorded.

Initially, to obtain bulk dust samples (referred to here as BD), all samples were sieved using a pre-cleaned, n-hexane rinsed  $250\text{ }\mu\text{m}$  mesh stainless testing sieve, covered with the lid and shaken for 3-5 min. After weighing, BD samples were fractionated into three different particle size fractions,  $125\text{-}250\text{ }\mu\text{m}$  (referred to as large particle size - P1),  $63\text{-}125\text{ }\mu\text{m}$  (referred to as medium particle size - P2) and  $25\text{-}63\text{ }\mu\text{m}$  (referred to as fine particle size - P3). Fractionation was achieved by using  $63\text{ }\mu\text{m}$ ,  $125\text{ }\mu\text{m}$ , and  $250\text{ }\mu\text{m}$  stainless sieves which were placed over each other and shaken by hand for 5-7 min. Following fractionation, the mass of each fraction was recorded.

### **2.3. Sample extraction and extract purification**

Analysis of PBDEs and NBFRs in fractionated and BD samples was conducted following the same extraction and clean-up as reported elsewhere (Al-Omran and Harrad, in press). Briefly, samples were spiked with internal standards (BDE-77, BDE-128,  $^{13}\text{C}$ -BDE-209,  $^{13}\text{C}$ -BTBPE and  $^{13}\text{C}$ -BEH-TEBP), extracted by ultrasonication with  $3 \times 2\text{ mL}$  n-hexane/acetone (3:1, v/v), evaporated to incipient dryness under a gentle nitrogen stream and resolubilised in  $1\text{ mL}$  n-hexane (Ali et al., 2011; van den Eede et al., 2012). For sample purification, the extract was fractionated into two fractions (F1 and F2) using  $2\text{ g}$  Florisil. F1 (containing PBDEs and DBDPE) was eluted with  $12\text{ mL}$  of hexane and F2 (containing the rest of the targeted NBFRs) was eluted with  $15\text{ mL}$  ethyl acetate. After evaporation to  $1\text{ mL}$ , a second purification step for F1 was conducted on  $2\text{ g}$  acid silica (44% w/w) and eluted with  $15\text{ mL}$  n-hexane/DCM (1:1, v/v). F2 was evaporated to dryness, resolubilised in  $3\text{-}5\text{ mL}$  of hexane, then evaporated to  $1\text{ mL}$ , and eluted with  $12\text{ mL}$  n-hexane/DCM (1:1, v/v) using an aminopropyl functionalised silica column ( $0.5\text{ g}$ ). F1 and F2 were combined and evaporated to incipient dryness, before resolubilisation in  $100\text{ }\mu\text{L}$  of iso-octane containing PCB-129 at  $250\text{ pg}/\mu\text{L}$  ready for GC/MS analysis (Al-Omran and Harrad, in press).

### **2.4. Instrumental analysis**

Analysis of our target compounds was performed using a gas chromatograph (GC) (Trace 1310 Gas Chromatograph) coupled to a mass spectrometer (MS) (ISQ Quadrupole MS); both (Thermo Fisher Scientific, USA). The GC was equipped with a programmable temperature vaporiser (PTV) injector and fitted with a capillary fused silica column (RESTEK, USA, 15 m x 0.25 mm inner diameter, 0.25  $\mu$ m film thickness). 2  $\mu$ L of purified extract were injected on the column. The inlet temperature was set at 92 °C. The GC oven temperature program was set at 50 °C for 0.5 min, ramp 20 °C/min to 240 °C, hold 5 min, ramp 5 °C/min to 270 °C, and ramp 20 °C/min to 305 °C, hold 19 min. Helium was used as a carrier gas with a flow rate of 1.5 mL/min. The MS was operated in ECNI mode. The electron lens voltage was set at 15 V and emission current set at 50  $\mu$ A. The ion source and transfer line temperatures were 300 °C and 320 °C respectively. BDE-77 was used as internal standard for quantification of BDE-28, PBEB, BDE-47, BDE-99, BDE-100; BDE-128 was used to quantify BDE-153, BDE-154 and BDE-183;  $^{13}$ C-BTBPE for BTBPE and EH-TBB;  $^{13}$ C-BEH-TEBP for BEH-TEBP; and  $^{13}$ C-BDE-209 used for BDE-209 and DBDPE.

## **2.5. QA/QC**

All glassware were cleaned by soaking in an alkali solution overnight, before rinsing with tap water, followed by deionised water, baking at 450 °C for 4.5 h, cooling, washing with acetone, and covering with aluminium foil until use. To assess any possible contamination during sample preparation and analysis method, one laboratory blank was processed in parallel with every set of 6 dust samples. In total 8 blanks were conducted. In none of these were any of the target compounds detected, and hence data are not corrected for blank concentrations. Similar results were obtained for field blanks (n=5). These consisted of sodium sulphate that spread on aluminium foil, collected using the vacuum cleaner and treated as a sample. For on-going evaluation of accuracy, an aliquot of SRM2585 was analysed with every 15 samples (or part thereof). The obtained data compared favourably with certified concentrations where provided and with previously reported data for this SRM where certified concentrations were not available, (Tables S1 and S2, Supplementary Data). Recoveries of internal standards ranged from 76 to 91 % in all dust samples (Table S3, Supplementary Data). Limits of detection (LOD) were estimated based on a signal to noise ratio 3:1, with limits of quantification (LOQ) estimated based on signal to noise ratio of 10:1, (Table S4, Supplementary Data)

## **2.6. Determination of organic carbon content in dust**



The total organic carbon (TOC) content of the dust samples was obtained by using a Total Organic Carbon analyzer TOC-V<sub>CSH/CSN</sub> fitted with a Solid Sample Module SSM-5000, both from SHIMADZU, Japan. The instrument provided measurements of Total Carbon (TC) and Inorganic Carbon (IC), hence the TOC was deduced by subtracting the IC value from TC. Due to the low dust mass available from H5 for fractionation and BFR analysis, TOC was not determined in dust samples from this house.

## **2.7. Statistical analysis**

Statistical analysis of the data was performed using Microsoft Excel 2013 and IBM SPSS statistics software (V. 20). The distribution of the concentration data for target pollutants was tested using the Shapiro-Wilk test. This revealed concentrations of all our target BFRs to be log normally distributed. Hence, data were log-transformed prior to comparison of means via T-test and One-way Repeated Measures ANOVA for testing significant differences between arithmetic means. For the purposes of statistical evaluation, all concentrations below LOQ were assigned a value of 0.5 LOQ. A *p* value < 0.05 was taken to indicate statistical significance.

## **3. Results and discussion**

### **3.1. Relationship between BFRs in different particle sizes**

In all dust samples analysed (n=40), BDE-47, BDE-99, BDE-153, BDE-209, BEH-TEBP, and DBDPE were found with detection frequencies of 100 %, while the detection frequency of other target compounds fell between 40-100%. Concentrations of BDE-28, BDE-100, BDE-154, and PBEB were very low, and they are thus excluded from statistical analysis for individual comparison. However, they were included in calculation of  $\Sigma_7$ tri-hepta-BDEs and  $\Sigma_5$ NBFRs.  $\Sigma_7$ tri-hepta-BDEs refers to the summation of seven congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183),  $\Sigma_5$ NBFRs represent the sum of PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE, with  $\Sigma$ BFRs equalling the sum of  $\Sigma_7$ tri-hepta-BDEs, BDE-209 and  $\Sigma_5$ NBFRs. Of all target compounds, BDE-209 was the predominant congener making average percentage contributions to  $\Sigma$ BFRs of 74.3%, 77.3%, 69.2%, and 62.7% in BD, P1, P2 and P3 dust samples respectively.  $\Sigma_5$ NBFRs contributed 24.2%, 21.5%, 29.1% and 35.3%  $\Sigma$ BFRs, while  $\Sigma_7$ tri-hepta-BDEs represented 1.5 %, 1.2 %, 1.7 %, and 2.0 % of  $\Sigma$ BFRs. Of the target NBFRs, BEH-TEBP predominated, with corresponding mean percentage contributions to  $\Sigma_5$ NBFRs of 76.9%, 75.1%, 83.1%, and 83.9%, followed by DBDPE with percentages 20.1 %, 21.9 %, 14.1 % and 13.9 % in BD, P1,

P2 and P3 dust samples respectively. EH-TBB and BTBPE were the least abundant of the target NBFRs, with EH-TBB comprising 0.95 %, 1.08 %, and 1.05 % and 0.79%  $\Sigma_5$ NBFRs, and BTBPE 1.94%, 1.74%, 1.64% and 1.24%  $\Sigma_5$ NBFRs in BD, P1, P2 and P3 respectively. Figure 1 shows average concentrations of  $\Sigma_7$ tri-hepta-BDEs, BDE-209, and  $\Sigma_5$ NBFRs in BD, P1, P2 and P3, additionally, Figure 2 illustrates concentrations and profiles of tri-hepta-BDEs and NBFRs.

As hypothesised and consistent with our previous study in Iraq (Al-Omran and Harrad, in press), BFR concentrations in elevated surface dust exceeded those in floor dust. The t-test analysis revealed that with the exception of DBDPE ( $p = 0.978$ ), our target compounds in elevated surface dust exceeded significantly those in floor dust with  $p$  values  $< 0.002$  for each of the three different particle size fractions and bulk dust. Average concentrations in ESD exceeded those in FD by the following factors: for  $\Sigma_7$ tri-hepta-BDEs, 2.4, 2.5, 3.2 and 2.9, for BDE-209, 1.4, 1.6, 1.4, and 1.3, and for  $\Sigma_5$ NBFRs, 2.9, 3.6, 4.7 and 4.6 in BD, P1, P2 and P3 respectively. Figure S1 (supplementary data) compares mean concentrations of  $\Sigma_7$ tri-hepta-BDEs, BDE-209 and  $\Sigma_5$ NBFRs in three particle sizes and bulk dust for both floor dust (FD) and elevated surface dust (ESD).

### 3.2 Distribution patterns of PBDEs and NBFRs with particle size

The average mass percentage of dust fractions P1, P2 and P3 were about 20.6%, 32.7% and 46.6%, respectively. In other words, on average ~79% of the bulk dust mass was associated with particles  $< 125 \mu\text{m}$ , which is comparable to the 80% figure reported for indoor dust particles  $< 150 \mu\text{m}$  (Wei et al., 2009). Figure S2 (supplementary data) illustrates the mass percentage contribution of dust fractions P1, P2 and P3 to BD.

Table 1 provides a statistical summary of concentrations of PBDEs in BD, P1, P2 and P3 respectively, with the equivalent data for NBFRs provided in Table 2. Following log transformation of BFR concentrations (ng/g dw), one-way repeated measures ANOVA was applied to test the hypothesis that concentrations of BFRs in P3 would exceed significantly those in P2 and P1. This analysis revealed no significant differences ( $p > 0.05$ ) between concentrations in different dust particle size fractions of: BDE-209, BTBPE, DBDPE, and EH-TBB. In contrast, in the finest particle size fraction (P3), concentrations of BDE-47 ( $p = 0.03$ ), BDE-99 ( $p = 0.004$ ), BDE-183 ( $p = 0.046$ ), BEH-TEBP ( $p = 0.001$ ),  $\Sigma_5$ NBFRs ( $p = 0.008$ ), and  $\Sigma_7$ tri-hepta-BDEs ( $p < 0.001$ ) exceeded significantly those detected in the

coarsest fraction (P1). Concentrations of BDE-99 ( $p = 0.009$ ), BEH-TEBP ( $p = 0.017$ ),  $\Sigma_5$ NBFRs ( $p = 0.007$ ), and  $\Sigma_7$ tri-hepta-BDEs ( $p < 0.001$ ) in the finest particles (P3) significantly exceeded those in the medium particle size fraction P2. In addition, concentrations in P3 of BDE-183 ( $p = 0.053$ ) were near-significantly elevated over those in P2. Moreover, BDE-99 ( $p = 0.008$ ), BDE-153 ( $p = 0.002$ ) BHH-TEPB ( $p = 0.003$ ), and  $\Sigma$ tri-hepta-BDEs ( $p = 0.003$ ) in the medium particle size fraction (P2) exceeded significantly those in the coarsest size fraction (P1). These findings show that for some BFRs, concentrations will increase with decreasing particle size; while for other BFRs, such a relationship does not exist. Figure 3 illustrates the distribution of  $\Sigma_7$ tri-hepta-BDEs, BDE-209, BEH-TEBP and DBDPE in particle size fractions from elevated surface dust and floor dust samples from five homes.

Interestingly, concentrations of our target BFRs in bulk dust (25-250  $\mu\text{m}$ ) exceeded significantly those in one or more of the 3 particle size sub-fractions for BDE-153, BEH-TEBP, and  $\Sigma_7$ tri-hepta-BDEs only. This suggests that the use in many past studies of a relatively broad particle size range has likely not unduly influenced exposure assessment.

As semi-volatile organic compounds (SVOCs) and additive flame retardants, our target BFRs can be released from the products via volatilisation into surrounding air, depending on their vapour pressure ( $V_p$ ). Such volatilised BFRs may then undergo deposition to both suspended and settled indoor dust, with the relative partitioning between these two phases governed by the octanol-air partition coefficient ( $K_{OA}$ ) of the BFRs (Li et al., 2006; Weschler and Nazaroff, 2010). This volatilisation with subsequent deposition process will be more important for BFRs with higher vapour pressures/lower  $K_{OA}$  values. By comparison, the presence of less volatile BFRs may be governed more by other processes such as direct contact between BFR source and dust and abrasion of BFR source materials (Rauert and Harrad, 2015; Suzuki et al., 2009; Webster et al., 2009). These factors, combined with the fact that atmospheric deposition of BFRs to dust particles will be greater for finer particle sizes due to their greater surface area to volume ratio (Lewis et. al., 1999; Wei et al., 2009; Mercier et al., 2011); means that significantly higher concentrations on finer dust particles would be anticipated for more volatile BFRs, with this likely less influential for their less volatile counterparts. With the exception of BEH-TEBP – for which the available data on its vapour pressure suggests it would behave in the same way as BDE-209, BTBPE, and

DBDPE (see table S5 listing available data for key physicochemical properties of our target BFRs) - this is consistent with our data, that show higher concentrations of BDEs 47, 99, and BEH-TEBP in finer dust particles, but no particle size preference for BDE-153, BDE-209, BTBPE, DBDPE, and EHTBB.

### **3.3 Influence of organic carbon content of dust on BFR particle size distribution**

In addition to the particle surface area to volume/mass ratio, variations in organic carbon content between ESD and FD and between different particle size fractions could potentially influence BFR concentrations in both ESD versus FD and in different particle size fractions. Figure S3 illustrates TOC contents of different particle size fractions in both FD and ESD. That this is feasible, is underlined by the fact that significant positive linear correlations were observed between BFR concentrations in all samples and their corresponding total organic carbon (TOC) content, with R values ranging between 0.883 and 0.979 ( $p < 0.001$ ). We therefore examined our data to check whether normalising BFR concentrations to the organic carbon content of the dust fraction analysed, exerted any influence on our observations. We found that doing so, made no difference to our findings based on concentrations normalised to dry weight of dust alone. This is consistent with our previous findings comparing BFRs in ESD and FD in Iraq (Al-Omran and Harrad, in press), that differences in organic carbon content of dust cannot explain either the differences in BFR concentrations in ESD and FD, or the variation in BFR concentrations with particle size fraction. Figure S4 (Supplementary Data) shows BFR concentrations and their corresponding total organic carbon (TOC) content in different particle sizes in elevated surface dust and floor dust from the four homes for which this was possible.

## **4. Conclusions**

While based on a small number of homes, our findings suggest that BFR concentrations recorded in indoor dust samples are influenced by the particle size fraction analysed. However, there is substantial variation between different BFRs. Specifically, while concentrations of more volatile BFRs like  $\Sigma$ tri-hepta-BDEs are significantly higher in dust particles of 25-63  $\mu\text{m}$  diameter than in those of 125-250  $\mu\text{m}$  and 63-125  $\mu\text{m}$  diameter; concentrations of less volatile BFRs such as BDE-209, BTBPE, EH-TBB, and DBDPE do not differ significantly between different dust particle size fractions. This is consistent with hypotheses that less volatile BFRs enter dust predominantly via mechanisms that do not

display clear preference for any one particle size fraction, such as abrasion of and direct contact with flame retarded materials, Consistent with our previous research in Iraq, concentrations of most of our target BFRs in elevated surface dust exceed significantly those in floor dust from the same UK microenvironments. Variations in the organic carbon content of dust explain neither the higher concentrations of BFRs in elevated surface compared to floor dust, nor the higher concentrations of some BFRs in finer dust particles. Instead, our data suggest that it is the greater surface area to volume ratio of finer dust particles that accounts for their higher BFR concentrations. Despite our small sample size precluded meaningful human exposure assessment, the results of this research support the idea that human exposure assessment could be affected by the dust particle size fractions analysed, and more detailed study of this issue is recommended.

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